A NEW KIND OF TEST OF THE CORRESPONDENCE PRINCIPLE BASED ON THE PREDICTION OF THE ABSOLUTE INTENSITIES OF SPECTRAL LINES

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Abstract

The *correspondence principle* postulates a relation between the average rate at which energy is actually being discontinuously emitted by quantum transitions and the continuous rate of emission which would be calculated from the classical theory. The principle has hitherto been used to predict the *relative intensities* of spectral lines of similar origin. Since, however, the classical theory permits a claculation of absolute rates of energy emission, it should be possible to calculate from the correspondence principle the *absolute intensities* of spectral lines. In the present article, the correspondence principle is subjected for the first time to this new kind of absolute test, using Czerny's data on the intensities of the far infra-red lines Nos. 8, 9, and 10 in the pure rotational spectrum of the dipole HCl. Tests of this kind have not previously been easy to make owing to lack of information as to the experimental values of absolute intensities or lack of knowledge of the the atomic models involved. The agreement between experimental and calculated intensities is close enough greatly to increase our confidence in the correspondence principle, justify us in subjecting it to further tests, and lead us to hope that an exact quantitative formulation of the principle may be found.

I. Introduction

THE correspondence principle postulates a relation between the actual intensity of the light discontinuously emitted by the transitions of atoms from one quantum state to another, and the intensity of the light which would be continuously emitted on the basis of classical electromagnetics by the motion of the electric charges composing the atoms. The exact quantitative formulation of this relationship has not yet been discovered, although the problem has been specially considered by Kramers,[1] Hoyt,[2] Van Vleck,[3] Tolman,[4] and others. Indeed except for the case of large quantum numbers it is not even certain thay any exact relationship necessarily exists. Nevertheless, the principle has proved of extraordinary value in ruling out the occurrence of quantum transitions when on the basis of the classical theory there would be no tendency

[1] Kramers, Kgl. Danske. Vidensk. Selsk. Skrifter **8, III,** 287 (1919).
[2] Hoyt, Phil. Mag. **46,** 135 (1923); *Ibid.* **47,** 826 (1924).
[3] Van Vleck, Phys. Rev. **24,** 334 (1924).
[4] Tolman, Phil. Mag. **49,** 130 (1925).

for the emission of radiation of the kind in question, and furthermore especially in the hands of Kramers (loc. cit.[1]) has permitted at least the approximate prediction of the relative intensities of a very considerable number of spectral lines. These successes of the correspondence principle make us hope that its range of application can be extended.

In all of the tests of atomic or molecular behavior to which the correspondence principle has hitherto been subjected it has only been feasible to compare the experimental facts either with the prediction that a given spectral line will not occur at all or with a prediction as to the *relative* intensities of related spectral lines. Nevertheless, since the classical theory provides us with a method of estimating the absolute rates with which energy is absorbed or emitted by moving charges, it should be possible to predict with the help of the correspondence principle the *absolute* intensity of absorption and emission lines.

It is the purpose of the present article to subject the correspondence principle to this new kind of more exacting test by comparing experimental and theoretical values for the strength of absorption lines of hydrogen chloride in the far infra-red. Such a test of predictions as to absolute intensities has not previously been possible, either because of the very limited number of spectral lines for which we know the absolute intensity, or because we did not have sufficient knowledge as to the atomic models involved. The recent beautiful work of Czerny,[5] however, on hydrogen chloride provides us with information as to the absorption of radiation accompanying changes in the velocity of rotation of a simple electric dipole, while the measurements of Zahn[6] coupled with the calculations of Pauling[7] give us a value for the electric moment of the dipole in question. As the result of the computations thus made possible, we find an agreement between experiment and theory, which is probably as close as could be expected with our present development of experimental technique and theoretical insight. This verification of a prediction as to absolute intensities cannot fail to increase our confidence in the correspondence principle, justify us in subjecting it to further tests and applications, and lead us to hope that the principle may sometime receive a correct and precise quantitative formulation.

Part I. Calculation of Absorption Coefficient

2. *Refinements in method of calculation.* Our first task will be to calculate from Czerny's absorption data the value of Einstein's coefficient

[5] Czerny, Zeits. f. Physik **34,** 227 (1925).
[6] Zahn, Phys. Rev. **24,** 400 (1924).
[7] Pauling, Proc. Nat. Acad. **12,** 32 (1926).

B_{ij} which gives the probability of transition from a lower quantum state S_i to a higher state S_j by the absorption of radiation. We shall then compare the experimental value of B_{ij} with that predicted by the correspondence principle.

The method of calculating values of B_{ij} and the results obtained in a wide variety of cases are illustrated by an earlier paper of Tolman.[8] In these earlier calculations, however, the difference in the energy levels corresponding to states S_i and S_j was so large that the number of molecules in the upper state S_j was relatively very small and the reinforcement of the primary beam by induced transitions from the upper to the lower state could be neglected. Our present treatment will be refined to cover this point, since the number of molecules in the upper quantum states under consideration is large enough so that the induced emission is in the neighborhood of fifty percent of the primary absorption.

The treatment will also be modified in the direction of greater precision by not introducing into the theoretical development the assumption that the effective width of the line is small as has hitherto been customary. In the numerical application of the theory to the data in hand, however, we shall find it possible to introduce this simplification.

3. *Einstein's treatment of absorption and emission.* Calculations of the kind to be made must be based on Einstein's 1917 formulation[9] of the nature of the absorptive and emissive processes. In accordance with this formulation, if we consider a system containing N_i molecules in the lower quantum state S_i, and N_j molecules in the upper state S_j, surrounded by radiation of the frequency ν involved in the quantum transitions, we may write the following expressions governing the rates of passage of molecules between the states by interaction with radiation. For the passage of molecules from state S_i to S_j by absorption we have

$$-dN_i/dt = N_i\rho_\nu B_{ij} \tag{1}$$

where ρ_ν is the density of radiation of the frequency ν which can be absorbed, and the constant B_{ij} is Einstein's coefficient of absorption. And for the passage of molecules in the reverse direction, we may write

$$-dN_j/dt = N_jA_{ji} + N_j\rho_\nu B_{ji} \tag{2}$$

where the constant A_{ji} is Einstein's coefficient of spontaneous emission and the constant B_{ji} the coefficient of induced emission. Furthermore, as a result of Einstein's considerations we have the following relations connecting the coefficients

[8] Tolman, Phys. Rev. **23,** 693 (1924).
[9] Einstein, Phys. Zeits. **18,** 121 (1917).

$$A_{ji}=\frac{8\pi h\nu^3}{c^3}\frac{p_i}{p_j}B_{ij}\ ; \qquad B_{ji}=\frac{p_i}{p_j}B_{ij} \tag{3}$$

where p_i and p_j are the a priori probabilities of the two states. In applying the above equations to an absorption experiment to calculate the effect of the molecules of a medium on the transmission of a beam of light, it should be noted that each molecule which changes from the lower state S_i to the upper state S_j under the action of the light in accordance with Eq. (1) is to be regarded as abstracting a quantum of light $h\nu$ from the oncoming beam. On the other hand for the molecules which pass in the opposite direction in accordance with Eq. (2), a careful distinction must be drawn, since those dropping by spontaneous emission are to be regarded as giving off quanta $h\nu$ of random direction and phase, while those which go down by induced emission are to be thought of as giving quanta coherent with the stimulating radiation and hence reinforcing the primary beam.

4. *Modified formulation of absorption and emission.* The original formulation given above applies strictly only to a system in which the radiation that can be absorbed or emitted may be treated as having a single definite frequency ν, a condition of affairs which corresponds on the experimental side to a spectral line having no appreciable width and on the theoretical side to a system in which the molecules in a given quantum state all have exactly the same energy content. In actual systems, however, molecules in a given quantum state do not all have the same energy content, but owing to the effect of fields from neighboring molecules, to the velocity of thermal motion, and perhaps in a small degree to a fundamental lack of sharpness, the molecules in a given quantum state have a range of energies distributed around a most probable value. And hence in accordance with the fundamental equation $E=h\nu$ we obtain a range of energy changes and corresponding range in frequencies for a given quantum transition. Hence since the spectral lines in the case which we are to treat are rather broad compared with their absolute position in the frequency scale, it will be desirable to modify the original Einstein formulation.

The possibility and nature of a new formulation which will allow for the absorption or emission of a continuous range of frequencies has already been indicated by Pauli[10] and by Einstein and Ehrenfest,[11] and it is believed that the following set of relations is in agreement with their point of view. In these new relations we shall use small letters b_{ij}, a_{ji}

[10] Pauli, Zeits. f. Physik **18**, 272 (1923).

[11] Einstein and Ehrenfest, Zeits. f. Physik **19**, 301 (1923).

and b_{ji} for the probabilities of absorption and emission, and shall regard these quantities as continuous variables which may change as we pass across a spectral line. For any given frequency ν we shall then write for the rate of passage of molecules from the lower to the higher state

$$-\frac{d(\delta N_i)}{dt}=(\delta N_i)\rho_\nu b_{ij} \tag{4}$$

and for the passage in the opposite direction

$$-\frac{d(\delta N_j)}{dt}=(\delta N_j)a_{ji}+(\delta N_j)\rho_\nu b_j \tag{5}$$

where

$$\delta N_i=\frac{\partial N_i}{\partial \nu}\delta\nu \text{ and } \delta N_j=\frac{\partial N_j}{\partial \nu}\delta\nu \tag{6}$$

are the numbers of molecules in the two quantum states which have exactly the right configuration to interact with radiation of frequency in the range ν to $\nu+\delta\nu$. Furthermore we shall also write the relations

$$a_{ji}=\frac{8\pi h\nu^3}{c^3}\frac{p_i}{p_j}b_{ij} \text{ and } b_{ji}=\frac{p_i}{p_j}b_{ij} \tag{7}$$

connecting the coefficients,—relations which are sufficient to guarantee agreement with the Planck radiation law.

We shall further find it convenient to retain the original Einstein coefficients B_{ij}, A_{ji} and B_{ji} by regarding them as average values for the spectral line under consideration in accordance with the equations of definition

$$B_{ij}=\frac{1}{N_i}\int b_{ij}\delta N_i \; ; \qquad A_{ji}=\frac{1}{N_j}\int a_{ji}\delta N_j \; ; \qquad B_{ji}=\frac{1}{N_j}\int b_{ji}\delta N_j \tag{8}$$

5. *Relation between the coefficient B_{ij} and the absorption coefficient a_ν.* We may now apply the foregoing considerations to the interpretation of an absorption experiment. Consider a beam of light of total intensity I in ergs cm^{-2} sec^{-1}, and let us define the intensity for a given frequency by the equation

$$I_\nu=dI/d\nu \tag{9}$$

Let the beam of light fall on a layer of absorbing medium having a cross section of one square centimeter and a thickness dx, and containing per cubic centimeter δN_i molecules in a conditions to absorb radiation in the frequency range ν to $\nu+\delta\nu$ and δN_j in a condition to emit this fre-

quency. Since the density of radiation corresponding to the intensity I_ν is obviously given by the equation

$$\rho_\nu = I_\nu / c \tag{10}$$

where c is the velocity of light, we may evidently write, in accordance with Eqs. (4) and (5), for the rates at which molecules in the layer of unit cross section and thickness dx are passing from one condition to the other by absorption and induced emission the expressions

$$-\frac{d}{dt}(\delta N_i dx) = (\delta N_i dx)\frac{I_\nu}{c} b_{ij} \text{ and } -\frac{d}{dt}(\delta N_j dx) = (\delta N_j dx)\frac{I_\nu}{c} b_{ji} \tag{11}$$

For each molecular transition, however, one quantum of energy $h\nu$ is either absorbed or returned to the beam, so that we easily obtain from Eqs. (11) an expression for the net rate at which energy in the frequency range ν to $\nu+\delta\nu$ is absorbed from the beam because of its passage through the layer, and can write

$$-d(I_\nu \delta\nu) = (\delta N_i dx)\frac{I_\nu}{c} b_{ij} h\nu - (\delta N_j dx)\frac{I_\nu}{c} b_{ji} h\nu \tag{12}$$

By the rearrangement of (12) and introduction of the expression for b_{ji} given by (7) we obtain

$$-\frac{1}{I_\nu}\frac{dI_\nu}{dx} = \frac{h\nu b_{ij}}{c}\left(\frac{\delta N_i}{\delta\nu} - \frac{p_i}{p_j}\frac{\delta N_j}{\delta\nu}\right) \tag{13}$$

and this is evidently the ordinary absorption coefficient for light of frequency ν which may be appropriately designated by the symbol α_ν giving us

$$\frac{h\nu b_{ij}}{c}\left(\frac{\delta N_i}{\delta\nu} - \frac{p_i}{p_j}\frac{\delta N_j}{\delta\nu}\right) = \alpha_\nu \tag{14}$$

If now we assume a condition of thermal equilibrium we may write in accordance with the Maxwell-Boltzmann distribution law

$$\delta N_j = \delta N_i \frac{p_j}{p_i} e^{-h\nu/kT} \tag{15}$$

and by substitution and rearrangement obtain in accordance with the definition of B_{ij} given by (8)

$$B_{ij} = \frac{1}{N_i}\int b_{ij}\delta N_i = \frac{c}{hN_i}\int \frac{\alpha_\nu d\nu}{\nu(1-e^{-h\nu/kT})} \tag{16}$$

where the integration is to be taken across the effective width of the absorption line. This would seem to be an exact expression for B_{ij} which is the average value of the coefficient b_{ij}, and is the quantity to be compared with that obtained from the correspondence principle.

6. *Calculation of B_{ij} from Czerny's results.* In the far infra-red Czerny (loc. cit.[5]) has measured the absorption of hydrogen chloride gas corresponding to simple changes in the state of rotation of the electric dipole H^+Cl^-. In particular he gives a plot of percentage transmission as a function of wave-length in the region of lines 8, 9, and 10 which correspond to changes in the rotational quantum number m of ($7\frac{1}{2}$ to $8\frac{1}{2}$), ($8\frac{1}{2}$ to $9\frac{1}{2}$) and ($9\frac{1}{2}$ to $10\frac{1}{2}$), and although he states that exact information as to the intensities of absorption and width of line cannot be taken from the plot owing to the relatively great width of his spectrometer slit, nevertheless his results would seem to be approximately reliable. Furthermore, he states that the length of his absorption tube was 12 cm, while for the three lines in question he appears to have used hydrogen chloride gas at one atmosphere pressure and room temperature. We thus have for the three lines mentioned all the data necessary for substitution in Eq. (16).

Since, even for these lines in the far infra-red, the effective width of the lines is not great compared with their absolute position in the frequency scale, we can rewrite Eq. (16) for our purposes in the approximate form

$$B_{ij}=\frac{c}{hN_i\nu_0\left(1-e^{-h\nu_0/kT}\right)}\int \alpha_\nu d\nu \tag{17}$$

where ν_0 is the frequency of the center of the line.

The number of molecules N_i in different states of rotation corresponding to different rotational quantum numbers

$$m=1/2,\ 3/2,\ 5/2,\ \ldots\ (i-1/2) \tag{18}$$

can be calculated in accordance with the Maxwell-Boltzmann distribution law from the equation[12]

$$N_i=\frac{Np_ie^{-\epsilon i/kT}}{\sum_i p_ie^{-\epsilon i/kT}}=N\frac{2ie^{-(i-\frac{1}{2})^2h^2/8\pi^2JkT}}{\sum_i 2ie^{-(i-\frac{1}{2})^2h^2/8\pi^2JkT}} \tag{19}$$

and for high temperatures may introduce the approximation

$$\sum_i 2ie^{-(i-\frac{1}{2})^2h^2/8\pi^2JkT}=\sum_i 2ie^{-(i-\frac{1}{2})^2\sigma}\approx(1/\sigma)\left[1+\tfrac{1}{2}\sqrt{\pi\sigma}\right] \tag{20}$$

[12] See Tolman, Phys. Rev. **22**, 470 (1923).

where N the total number of molecules per cc at one atmosphere and 20°C, can be taken as 2.52×10^{19} and the term containing J, the moment of inertia of the molecule can be taken from Czerny's own work which gives $h/8\pi^2J=10.397\ c$. The results for the three lines nos. 8, 9, and 10 are given in column two of Table I.

Values for the wave numbers ν_0/c corresponding to the centers of the lines were obtained by Czerny as given in column three, and values of the factor $(1-e^{-h\nu_0/kT})$ have been calculated and are given in column four of Table I.

Finally the values of the integral $\int \alpha_\nu d\nu$ have been obtained from Czerny's plot of percentage transmission I/I_o as function of wave-length λ by replotting log I/I_o against $1/\lambda$ and with the help of a graphical integration substituting into the equation

$$\int \alpha_\nu d\nu = -\frac{2.30c}{x}\int \log\frac{I}{I_0}\,d\left(\frac{1}{\lambda}\right) \tag{21}$$

where for x we use the length of the absorption tube 12 cm. The values obtained are given in column five of Table I.

We now have all the quantities necessary for substitution into Eq. (17) and obtain for B_{ij} the results given in the last column of Table I.

TABLE I

(c. g. s. units)

No. of line	N_i	ν_0/c	$(1-e^{-h\nu_0/kT})$	$\int \alpha_\nu\, d\nu$	B_{ij}
8	0.9806×10^{18}	165.63	0.5553	3.318×10^{10}	5.61×10^{16}
9	$4.897\ \times10^{17}$	185.86	0.5970	0.425×10^{10}	6.81×10^{16}
10	$2.180\ \times10^{17}$	206.38	0.6356	1.987×10^{10}	10.59×10^{16}

PART II. THEORETICAL CALCULATIONS OF THE ABSORPTION COEFFICIENTS

7. *Application of the correspondence principle to a dipole rotator.* We must now turn our attention to the theoretical estimation of the above absorption coefficients with the help of the correspondence principle, which postulates a relation between the rates at which energy is actually emitted by molecules in accordance with the quantum theory and the rates which would be calculated on the basis of the classical theory.

Consider a system containing a number of dipole rotators all in the same quantized state of rotation S_j corresponding to the rotational quantum number m_j. It we treat the system as degenerate, i.e. not spatially quantized, the axes of rotation of these dipoles will be oriented in random directions, and the emission of radiation will result from a jump to a lower state of rotation S_i corresponding to the rotational quantum number $m_i=m_j-1$, the axis of rotation for any particular dipole retaining its direction in space.

On the basis of the *quantum theory* the average rate of emission of energy per rotator will evidently be

$$\left(\frac{dR}{dt}\right)_Q = A_{ji}h\nu \tag{22}$$

where A_{ji} is Einstein's coefficient of spontaneous emission.

On the other hand, on the basis of the *classical theory* the rate of spontaneous emission of energy by a dipole rotator would be

$$\left(\frac{dR}{dt}\right)_{Cl} = 2\times\frac{16\pi^4}{3c^3}C^2\omega^4 \tag{23}$$

where C is the electric moment of the dipole and ω the frequency of revolution.

The *correspondence principle* postulates now the existence of a relation between such pairs of expressions for the rates of energy emission, as given by the two theories. As already stated the exact formulation of this relation if it exists has not yet been discovered. It seems reasonable, however, to presume that the correct quantum theory rate of emission as given by Eq. (22) might be determined by some method of averaging the classical rates which in accordance with Eq. (23) would be calculated for the initial and final states of the rotator or perhaps for the mechanically possible intermediate states. This presumption can be symbolically expressed by the equation

$$\frac{dR}{dt} = A_{ji}h\nu = 2\times\frac{16\pi^4}{3c^3}[C^2\omega^4]_{av} = 2\times\frac{16\pi^4}{3c^3}Q^2\nu^4 \tag{24}$$

where we have introduced for convenience a new quantity Q which may be regarded as the electric moment of an idealized classical rotator having the frequency ν and desired rate of energy emission $A_{ji}h\nu$.

8. *Methods of averaging.* The method of averaging, which has received the most study and in the hands of Kramers (loc. cit.[1]) has led to excellent estimates of the relative intensities of lines, would either make the hypothetical electric moment Q merely the mean of the actual electric moments in the initial and final quantum states in accordance with the equation

$$Q = \frac{C_i + C_j}{2} \tag{K}$$

or would make the square of Q the mean of the squares of C_i and C_j in accordance with the equation

$$Q^2 = \frac{C_i^2 + C_j^2}{2} \tag{K}$$

Six methods of averaging over the mechanically possible intermediate states, one of which was proposed by Kramers, have also been studied by Hoyt (loc. cit.[2]) and by Tolman (loc. cit.[4]) and are represented by the following equations

$$Q^2=\int_0^1 C^2 d\lambda \tag{A}$$

$$Q=\int_0^1 C\, d\lambda \tag{B}$$

$$\log Q=\int_0^1 \log C\, d\lambda \tag{C}$$

$$Q^2\nu^4=\int_0^1 C^2\omega^4\, d\lambda \tag{D}$$

$$Q\nu^2=\int_0^1 C\omega^2\, d\lambda \tag{E}$$

$$\log (Q\nu^2)=\int_0^1 \log (C\omega^2) d\lambda \tag{F}$$

where λ is an auxiliary variable which is related to the phase integral ($I=\int pdq$) taken for intermediate states by the equation

$$I=I_i+\lambda(I_j-I_i) \tag{25}$$

Since for a *rigid* dipole the electric moment is a constant, four of the methods of averaging evidently lead to a simple equality of the hypothetical moment Q and the actual moment C, as shown in Table II.

TABLE II

Method of Average K, A, B, C	Value of Q^2 for transition $(m+1)$ to m $Q^2=C^2$
D	$\frac{16}{5}\frac{(m+1)^5-m^5}{(2m+1)^4}C^2$
E	$\frac{16}{9}\frac{\{(m+1)^3-m^3\}^2}{(2m+1)^4}C^2$
F	$\frac{16}{\epsilon^4}\frac{(m+1)^{4(m+1)}}{m^{4m}(2m+1)^4}$

[13] See Tolman, *loc. cit.*, footnote 4. The treatment given in this article was worded so as to apply to a rigid dipole rotator with whole quantum numbers. The results quoted, however, are the same for the case of whole and half quantum numbers.

The results for the other three methods of averaging in terms of the rotational quantum numbers m and $m+1$ of the two states have previously been published[13] and are also given in Table II.

Substituting the values for m (7.5, 8.5 and 9.5), corresponding to the three lines under investigation, into the expression given by methods D, E, and F of averaging, we find that these methods also give within one percent the same value

$$Q^2 = C^2 \tag{26}$$

and hence we shall use this in our following calculations. It is indeed fortunate that we have data to test so simple a case as that of a rigid dipole rotator, since it seems probable that for any reasonable method of averaging, expression (26) would give at least the right order of magnitude for Q^2.

9. *Relation between B_{ij} and Q^2.* To calculate the theoretical value of Einstein's coefficient of absorption B_{ij} from the value of Q^2 we have merely to combine Eqs. (3) and (24) in the text and obtain

$$B_{ij} = 2 \times \frac{2\pi^3}{3h^2} \frac{p_j}{p_i} Q^2 \tag{27}$$

10. *Numerical value of Q and theoretical values of B_{ij}.* The measurements by Zahn[6] of the dielectric constant of hydrogen chloride gas make it possible to calculate the electric moment of the dipole and this has been done by Pauling[7] in accordance with the theory of half quantum numbers. He obtains the value 0.3316×10^{-18} in C.G.S. electrostatic units.

Taking this as the value of Q and substituting in Eq. (27) we obtain for B_{ij} the values 10.9, 10.8, and 10.7×10^{16} for the successive lines Nos. 8, 9, and 10.

11. *Application of correspondence principle treating the system as non-degenerate.* In the foregoing calculations, as noted above, we have treated the dipole rotators as degenerate systems, with their axes of rotation distributed in random directions. It has been suggested by Kemble,[14] however, in considering rotation-oscillation spectra, that the correspondence principle ought to be applied to such systems by treating them as though they had been made non-degenerate by spatial quantization in a weak external (magnetic) field.

Under these circumstances, the axes of rotation can only assume certain spatially quantized directions and we must use two quantum numbers to describe the state of the rotator, a rotational quantum number m

[14] Kemble, Phys. Rev. **25**, 1 (1925).

which is proportional to the total angular momentum of the rotator, and an equatorial quantum number r which is proportional to the component of the angular momentum parallel to the applied field, the angle between the axis of rotation and the external field being given by the equation $\cos\theta = r/m$. The possible absorption processes may then be correlated with a change in the rotational quantum number from m to $m+1$ and changes in the equatorial quantum number from r to $r \pm 1, 0$. Furthermore each of these processes may be correlated with terms in the Fourier analysis for the motion of the rotator, and the frequency of occurrence of the different transitions estimated from the magnitude of the coefficients of the corresponding terms in the Fourier analysis.

We have also made an estimation of the intensities of the three lines in question on this basis. The calculation is complicated by the fact that the Fourier coefficients corresponding to a given quantum transition now have in general different magnitudes in the initial and final state of the molecule, since they depend on the angle between the external field and the axis of rotation and in general this changes when the transition occurs. In order to overcome this difficulty, following the procedure of Kemble, we have determined the Fourier analysis for an intermediate motion, in which the angle between the external field and axis of rotation is given by the equation $\cos\theta = \bar{r}/\bar{m}$, where $\bar{r}$ and $\bar{m}$ are the respective means of the values of the quantum numbers r and m in the initial and final state. We have then used the Fourier coefficients of the proper terms in the analysis of this intermediate motion as the amplitudes of the idealized classical motions of frequency ν which on the basis of the correspondence principle may be assumed to give the same rate of energy emission as the average rate given by the quantum transition in question.

We do not reproduce the calculations here, since they are somewhat lengthy, and for the particular absorption lines under consideration lead nearly to the same results as our previous simpler calculations which treated the rotators as degenerate systems. The approximate agreement of these new results obtained by treating the rotators as non-degenerate is due to the fact that the theory of spatial quantization prescribes no less than sixteen values of the angle between field direction and precessing axis even for the molecules of lowest energy content involved in the production of lines Nos. 8, 9, and 10, and the changes in direction of the axis accompanying the permitted transitions are small. Hence the spatially quantized system of rotators behaves nearly the same as a degenerate system in which the axes of rotation are uniformly distributed in direction and there is no change in direction when a quantum transition takes place. For the first lines in the rotational spectrum the two methods of

treatment lead to quite different results. For this reason an experimental determination of the intensities of these lower lines would be interesting.

12. *Newer methods of treatment.* In addition to the methods of applying the correspondence principle discussed above, there has recently been considerable investigation of the calculation of intensities by methods specially adapted to agree with the Burger Dorgelo "sum rule" for the intensities of the components of a multiplet line. These methods may be called with Fowler "refined applications" of the correspondence principle. In particular Professor J. H. Van Vleck has been good enough to call our attention by letter to an article by Reiche and Thomas[15] in which an expression has been obtained for the absolute intensity of the pure rotational lines for a dipole rotator. It is interesting to note that their expression (see page 521 l.c.) becomes identical with our equation (27) obtained from methods of averaging K, A, B, C, provided we modify their equation in such a way as to allow for the fact that the electric separation in the hydrogen chloride molecule is different from the internuclear distance, and further substitute the same a-priori weights which we have employed. Hence we may regard our calculations as also agreeing with the work of Reiche and Thomas.

It should also be noted that the new quantum mechanics of Born and Heisenberg is specially adapted for the calculation of intensities of lines, but we have not yet carried through a calculation along these lines. To do this, it would first be necessary to consider whether, by going over to the new basis, modifications might not have to be introduced into Pauling's calculation of electric moment.

PART III. COMPARISON OF EXPERIMENTAL AND THEORETICAL VALUES OF B_{ij}

13. *Conclusion.* We may now compare the experimental values of B_{ij} calculated from Czerny's absorption measurements with the theoretical values calculated from the correspondence principle, as given below in the last two columns of Table III.

TABLE III

No. of line	Transition	B_{ij}(exp.)	B_{ij}(theor.)
8	$m = 7.5$ to $m = 8.5$	5.6×10^{16}	11.9×10^{16}
9	$m = 8.5$ to $m = 9.5$	6.8×10^{16}	11.8×10^{16}
10	$m = 9.5$ to $m = 10.5$	10.6×10^{16}	11.6×10^{16}

The agreement is not exact, and perhaps outside the experimental error of the two sets of measurements of Czerny and Zahn which were used in the calculations. Nevertheless when we consider the difficulties

[15] Reiche and Thomas, Zeits. f. Physik, **34**, 510 (1925).

of both kinds of experimental work and the complexity of the three calculations by which the electric moment was obtained from the measurement of dielectric constant, and Einstein's coefficient was calculated first from the absorption measurements and then from the correspondence principle, the results are certainly of a nature to increase our respect for the correspondence principle, which has now been subjected for the first time to this kind of *absolute* test, involving the absolute rather than the relative intensities of spectral lines.

The most striking characteristic of the lack of agreement is the gradual rise in the experimental values of B_{ij} as we go to higher quantum numbers approaching perhaps the nearly constant value predicted from the correspondence principle. This may indicate the necessity of a progressive modification of the correspondence principle as we go to lower quantum numbers, a possibility which finds some support from other directions. Speculations, however, as to the precisely correct manner of applying the correspondence principle can best be postponed until more certain experimental data are at hand. An attempt to obtain further data for this purpose is already under way in this laboratory.

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